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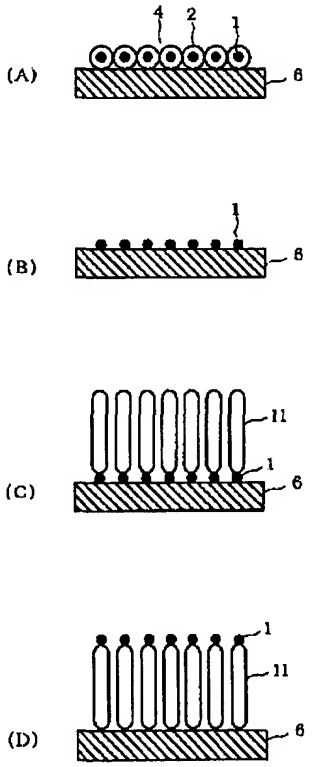
(54)【発明の名称】　カーボンナノチューブ

(57)【要約】
【課題】　基板表面に直接合成・成長され、しかも高密度、高精度で配列されたカーボンナノチューブを提供する。
【解決手段】　内腔を有しその周囲をタンパク質２で覆った分子４であって、前記内腔部に無機材料原子１を保持させた該分子を基板上６に展開配置した後、該タンパク質を除去することによって基板上に残存する前記無機材料原子１を種として合成してなるカーボンナノチューブ１３である。タンパク質分子４はウイルス、フェリチンファミリー（フェリチンやアポフェリチン）、ＤｐｓＡタンパク質あるいはＭｒｇＡタンパク質であり、無機材料原子１は鉄、鉄酸化物等の鉄化合物、ニッケル、ニッケル酸化物等のニッケル化合物、コバルト、コバルト酸化物等のコバルト化合物のいずれかであり、合成方法はＣＶＤ法であってもよい。



【特許請求の範囲】
【請求項1】 内腔を有し、その周囲をタンパク質で覆った分子であって、前記内腔部に無機材料原子を保持させた前記分子を基板上に展開配置した後、前記タンパク質を除去することによって基板上に残存する前記無機材料原子を種として合成してなるカーボンナノチューブ。
【請求項2】 タンパク質分子がウイルスであることを特徴とする請求項1記載のカーボンナノチューブ。
【請求項3】 タンパク質分子がフェリチンファミリーであることを特徴とする請求項1記載のカーボンナノチューブ。
【請求項4】 フェリチンファミリーがフェリチンまたはアポフェリチンであることを特徴とする請求項3記載のカーボンナノチューブ。
【請求項5】 タンパク質分子がDpsAタンパク質またはMrgAタンパク質であることを特徴とする請求項1記載のカーボンナノチューブ。
【請求項6】 無機材料原子が鉄、鉄酸化物、その他の鉄化合物、ニッケル、ニッケル酸化物、その他のニッケル化合物、コバルト、コバルト酸化物、その他のコバルト化合物のいずれか1種であることを特徴とする請求項1～5のいずれかに記載のカーボンナノチューブ。
【請求項7】 合成方法がCVD法であることを特徴とする請求項1～6のいずれかに記載のカーボンナノチューブ。
【発明の詳細な説明】
【0001】
【発明の属する技術分野】本発明は、カーボンナノチューブに関し、特に、基板表面に高密度で、しかも高精度で配列されたカーボンナノチューブに関する。
【0002】
【従来の技術】カーボンナノチューブは、高いアスペクト比を有すると共に、先端の曲率半径が小さいため、電解放出型電子エミッタ（冷陰極装置）における電子放出源の構成材料（冷陰極材料）として適している。
【0003】例えば、多数本を束ねたカーボンナノチューブから、64Vという低いターンオン電圧で、400μA／cm²と言う高い放出電流密度が得られることが報告されている。
【0004】このように低電圧駆動の大電流電子線放出源としての適用が注目されるカーボンナノチューブは、今日まで、その合成技術や応用技術等に関する提案や報告が幾つかなされている。
【0005】例えば、カーボンナノチューブを冷陰極部材として利用する電界放出型エミッタをフラットパネルディスプレイに適用するためには、カーボンナノチューブをできるだけ配向させ、できれば電極面に垂直に配向することが望ましく、できれば蛍光体に対応して2次元アレイ状に配置することが望ましい。この配列技術に関し、次のような報告や提案がある。
【0006】Walt de Heer et al.によるScience誌268巻（1995）845頁では、カーボンナノチューブの懸濁液をセラミックフィルターに流してフィルター表面にカーボンナノチューブを配列させ、これをプラスチックシート上に転写して、該シート上に面垂直または面内に配向したカーボンナノチューブの層を形成する技術を開示している。
【0007】また、特開平10-149760号公報は、電界放出型冷陰極装置における電子エミッタ材としてカーボンナノチューブを使用する技術を開示しており、支持基板上に複数の電子エミッタを形成するにあたり、例えば、アーク放電によってアノード電極の炭素を昇華させ、それをカソード上に析出させて形成したカーボンナノチューブを、塗布・分散等して基板上に倒木が重なり合うようにして配置させることにより各々の電子エミッタを構成する技術を開示している。
【0008】特開平10-12124号公報は、電子エミッタとして使用するカーボンナノチューブを、陽極酸化膜中に規則正しく配設した細孔の中に析出させた金属触媒の作用により成長させる技術を開示している。
【0009】更に、日本画像学会（The Society of Electrophotography of Japan）発行「Pan-Pacific Imaging Conference／Japan Hardcopy '98」（1998年7月15～17日開催）313～316頁は、電界放出型電子エミッタとして機能させるカーボンナノチューブを、電気泳動法により印加電界方向に配列させ、基板上に形成したポリシラン等で構成される保持部材に移動させて固定する技術を開示している。
【0010】
【発明が解決しようとする課題】しかし、以上の報告や提案はいずれも、カーボンナノチューブを別途作製しておき、これを基板上に配列・固定する技術であって、生産性は必ずしも良好とは言えないばかりか、基板上に配向して高密度で、かつ（例えば、蛍光体に対応させた2次元アレイ状の配置等、所望位置への）高精度での配列・固定も必ずしも容易とは言えないし、また電子線放出源として理想的な基板面への垂直配置についても問題が多々ある。
【0011】本発明は、基板上に直接合成されるカーボンナノチューブであって、しかもその合成が、カーボンナノチューブの高密度・高精度での配列・固定および基板面への理想的な垂直配置を容易に実現することができるカーボンナノチューブを提供することを目的とする。
【0012】
【課題を解決するための手段】上記目的を達成するために、本発明のカーボンナノチューブは、内腔部に無機材料原子を保持し、その周囲をタンパク質で覆った分子を、基板上に展開配置した後、タンパク質を除去するこ

とによって基板上に残存する無機材料原子を種として合成してなることを特徴とする。

【0013】また、本発明のカーボンナノチューブは、（1）上記のタンパク質分子が、①ウイルス（例えば、アデノウィルス、ロタウィルス、ポリオウィルス、HK97、CCMV等）、②フェリチンやアポフェリチンのようなフェリチンファミリー、③DpsAタンパク質やMrgAタンパク質（プロテイン・データ・バンク参照）であってもよいし、（2）上記の無機材料原子が鉄、鉄酸化物、その他の鉄化合物、ニッケル、ニッケル酸化物、その他のニッケル化合物、コバルト、コバルト酸化物、その他のコバルト化合物のいずれか1種であってもよく、（3）上記の合成方法がCVD法であってもよい。

【0014】

【発明の実施の形態】本発明では、先ず、内腔部に無機材料原子を保持しその周囲をタンパク質で覆った分子（以下、「タンパク質分子」と記すこともある）を、基板上に、高密度かつ所望位置に高精度（本発明において、「高精度」と記すときは、「所望位置に高精度」を意味する）で、展開配置（すなわち、2次元的に配列・固定）する。

【0015】このタンパク質分子は、例えば図1に模式的に示すように、無機材料原子の芯1を内腔部に保持し、この周囲をタンパク質の殻2で覆った金属タンパク質複合体であって、馬、牛等の動物のひ臓や肝臓等の臓器から取り出したフェリチンや、内腔に各種の無機材料原子を内包したアポフェリチン等が好ましく使用できる。

【0016】フェリチンの場合、芯1の無機材料原子は、通常は、酸化鉄（Fe_2O_3）で、芯1の直径は6nm程度、酸化鉄の総数は3000個程度であり、殻2は分子量2万程度のタンパク質の24量体で、24量体全体の外径は12nm程度である。

【0017】Dpsタンパク質の場合は、図示は省略するが、芯1の直径は4nm程度、殻2は正四面体の12量体で、12量体全体の外径は9nm程度である。

【0018】なお、本発明において、芯1の無機材料原子は、酸化鉄に限定されず、鉄、酸化鉄以外の鉄化合物、あるいはニッケル、コバルト、これらの酸化物や酸化物以外の化合物等であってもよい。

【0019】このタンパク質分子の2次元的な配列・固定は、例えば、特開平11-45990号公報に記載の方法で行われる。

【0020】具体的には、図2に示すように、タンパク質分子4を分散した緩衝液（溶液）（濃度40mM、pH5．3のリン酸バッファ溶液と、濃度40mMの塩化ナトリウム水溶液との等量混合溶液等）3の表面に、ポリペプチド膜5を張り、緩衝液3のpHを調節する（図2（A））。ポリペプチド膜5が正電荷を帯びているのに対し、タンパク質分子4は負電荷を帯びているため、時間の経過に伴ってタンパク質分子4がポリペプチド膜5に付着し、タンパク質分子4の2次元結晶ができる（図2（B））。

【0021】このポリペプチド膜5上に基板6を載置し（浮かべ）て、ポリペプチド膜5を基板6に付着させる（図2（C））。この基板6を取り出せば、ポリペプチド膜5を介して、タンパク質分子4の2次元結晶が付着した基板6を得ることができる（図2（D））。

【0022】あるいは、図3に示すように、タンパク質分子4を分散した溶液（純水、純水に塩化ナトリウム等の電解質物質を加えたもの等）3に基板6を入れ、この基板6を液面に垂直に徐々に引き上げると、基板6の両面に濡れ膜7が生じる。この濡れ膜7には、タンパク質分子4が2次元状に分散しているため、膜7が乾燥すれば、タンパク質分子4の2次元結晶が両面に付着した基板6を得ることができる。

【0023】また、図4に示すように、台8上に置いた基板6上に、垂直に白金ブレード9を立て、基板6とブレード9の間に、図2の場合と同様のタンパク質分子を分散した溶液3を表面張力でもたせ、ブレード9は固定し、台8すなわち基板6を一定速度で矢印方向に徐々に移動すると、基板6上に溶液3の薄膜7が生成する。この薄膜7には、タンパク質分子4が2次元状に分散しているため、膜7が乾燥すれば、タンパク質分子4の2次元結晶が一方の面に付着した基板6を得ることができる。

【0024】更には、図5（A）に示すように、図2の場合と同様のタンパク質分子4を分散した溶液3を注入した容器10内に基板6を、溶液3に対して垂直に（図示は省略するが、斜めでもよい）入れ、溶液3を容器10の上方からシリンジ（図示省略）等で一定速度で徐々に抜き出す（図示は省略するが、容器10の下方に孔を空けておき、この孔から重力等の作用により一定速度で徐々に抜き出してもよい）と、図5（B）に示すように、基板6の両面に濡れ膜7が生じる。この濡れ膜7には、図2の場合の濡れ膜7と同様に、タンパク質分子4が2次元状に分散しているため、膜7が乾燥すれば、タンパク質分子4の2次元結晶が両面に付着した基板6を得ることができる。

【0025】これら図2～5に示す方法において、タンパク質分子4の2次元結晶は、基板6の全面に形成してもよいし、特定の部分にのみ適宜のパターンで形成してもよく、後者の場合には、予め基板6表面に、タンパク質分子4が付着し易い領域と付着し難い領域（例えば、後述する処理方法により、疎水性領域と親水性領域）を作成しておいたり、基板6にタンパク質分子4を2次元状に付着させた後に、該分子4を適宜のパターンで除去する等の方法が採用される。

【0026】また、図6（A）～（D）に示すような、

吉村らにより開発された転写法（Ａｄｖ．Ｂｉｏｐｈｙｓ．Ｖｏｌ．３４，ｐ９９～１０７（１９８７）参照）による方法であっても、タンパク質分子４の２次元結晶膜を得ることができる。

【００２７】先ず、図６（Ａ）において、特定の溶液（濃度２％のシュークロース溶液）３に、タンパク質分子（酸化鉄を内包したアポフェリチン）４を、シリンジ１１等を用いて注入すると、タンパク質分子４は、図６（Ｂ）に示すように、シュークロース溶液３上に浮上する。

【００２８】最初に気液界面に到達したタンパク質分子４は、図６（Ｃ）に示すように、アモルファス膜１２′を形成し、後から到達したタンパク質分子４は、該膜１２′の下に付着し、図６（Ｄ）に示すように、該膜１２′の下に２次元結晶１２″を形成する。

【００２９】このアモルファス膜１２′と２次元結晶１２″とからなる膜１２の上に、図６（Ｄ）に示すように、基板６を載置すれば、このタンパク質分子の膜１２は基板６側に転写される。

【００３０】この膜１２は、基板６を疎水性に処理しておくことで、簡単に基板６側に転写することができる。

【００３１】基板６の疎水性処理は、例えば、シリコン基板では、ヘキサメチルジシラザン（ＨＭＤＳ）（$(CH_3)_3SiNHSi(CH_3)_3$）等で処理したり、ガラス基板では、フッ化炭素の単分子膜で覆ったりする等して行うことができる。

【００３２】この転写法においても、タンパク質の２次元結晶膜１２は、基板６の全面に形成してもよいし、また条件を選定すれば、膜１２は、疎水性領域にのみ転写し、親水性領域には転写しないようにすることができるため、予め基板６上に疎水性領域と親水性領域とを適宜のパターンで形成して、膜１２を適宜のパターンに作出することができる。

【００３３】本発明では、以上のようにして、タンパク質分子を２次元結晶状態で基板上に展開配置した後、タンパク質部分を除去し、タンパク質分子の内腔部に保持させた無機材料原子を、基板上に２次元的に出現させる。

【００３４】このタンパク質部分の除去は、一般には、熱処理によって行う。

【００３５】例えば、窒素等の不活性ガス中、４００～５００℃で、適宜の時間（例えば、１時間）保持すると、タンパク質部分や図２の場合のポリペプチド膜が焼失し、基板上には無機材料原子が２次元的に、高密度のドット状で、残存する。

【００３６】これを更に、水素等の還元ガス雰囲気中、５００～９００℃で、適宜の時間保持し、無機材料原子を還元してもよい。

【００３７】本発明のカーボンナノチューブは、上記のようにして、基板上に展開配置した無機材料原子（本発明において、「無機材料原子」と記すときは、その酸化物や他の化合物を含む意味である）を種として、基板上に直接、合成するものである。

【００３８】この合成方法は、カーボンナノチューブが合成できればどのような方法でもよいが、ＣＶＤ法が好ましく適用できる。

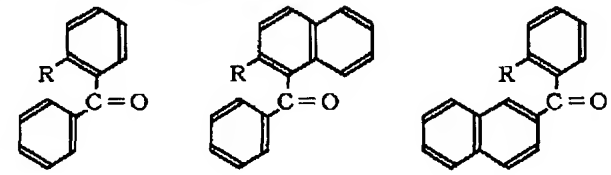
【００３９】すなわち、無機材料原子を展開配置した基板を密閉系内に置き、この密閉系内にカーボンナノチューブの原料となる有機化合物を導入し、基板温度を５００～９００℃にする。これにより、有機化合物が分解してカーボン粒子が発生し、このカーボン粒子が無機材料原子を種としてカーボンナノチューブを合成し、成長させる。

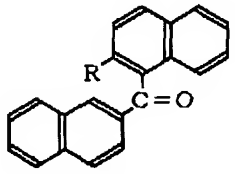
【００４０】本発明におけるＣＶＤ法は、減圧下（例えば、１Ｐａ未満～10^{-6}Ｐａ程度）で行うこともできる。

【００４１】また、カーボン源としては、有機化合物であれば、特に限定されないが、化１に示す芳香族ケトン化合物や、オルトメチルジアゾールケトン、フタロシアニン、その他の芳香族化合物、あるいは各種の脂肪族化合物等が好ましく使用できる。

【００４２】

【化１】





ただし、Ｒはアルキル基

【００４３】このＣＶＤ法は、例えば、図７に示すような装置を用いて行われる。

【００４４】図７において、密閉チャンバ２０内のヒータ２１上に基板６をセットし、真空ポンプ２２でチャンバ２０内を排気し、減圧しつつ（あるいは、パイプ２３から窒素やアルゴン等の不活性ガスをノズル２４より導入しつつ）、ヒータ２１で基板６を加熱する。

【００４５】基板６の温度が安定した後、切り替えバルブ２５を作動させて、カーボン源供給装置２６から上記のような有機化合物の蒸気を、窒素やアルゴン等のキャリアガスに同伴させて密閉チャンバ２０内に供給し、ノズル２４により基板６上に導く。

【００４６】この有機化合物の蒸気は、基板６上近傍において分解し、カーボン粒子を発生させて、基板６上の無機材料原子を種としてカーボンナノチューブを合成・成長させる。

【００４７】上記のＣＶＤ法にて、無機材料原子を種としてカーボンナノチューブを合成・成長させた後、同じ密閉チャンバ内、あるいは該チャンバから取り出して適宜の加熱手段にて、窒素やアルゴン等の不活性ガス雰囲気中、４００～９００℃で、１時間程度保持して、カーボンナノチューブのアニーリングを行えばよい。このアニーリングにより、種となる無機材料原子との密着性が良好となると共に、電気的導通性の向上を図ることができる。

【００４８】以上説明した本発明におけるカーボンナノチューブの合成・成長の状況を、順を追って、図８に、模式的に示す。

【００４９】先ず、図８（Ａ）に示すように、基板６上に、高密度・高精度で、タンパク質分子４（２次元結晶）を、展開配置する。

【００５０】次いで、この基板６を熱処理して、タンパク質分子４のタンパク質部分２を焼去し、図８（Ｂ）に示すように、該分子４の内腔部に保持されていた無機材料原子１を、基板６上に、高密度・高精度で、２次元的にドット状に残存させる。

【００５１】この状態の基板６を密閉系内に置き、ＣＶＤ法により、該系内に炭素蒸気を飛遊させると、基板６上の無機材料原子１を種として、カーボンナノチューブ１３が合成・成長する。その成長方向は図８（Ｃ）に示すように上方向の場合と図８（Ｄ）に示すように下方向の場合がある。

【００５２】これを適宜の加熱手段にてアニーリング処理して、本発明のカーボンナノチューブを得る。

【００５３】なお、図８では、基板６の片面に、タンパク質分子４、無機材料原子１が付着して、カーボンナノチューブ１３が合成・成長する態様を示したが、基板６の両面にこれら４，１が付着し、カーボンナノチューブ１３が合成・成長するものであってもよい。

【００５４】このように、本発明においては、基板６面に展開配置される無機材料原子（６ｎｍ）が、所定の間隔（約１２ｎｍ間隔）でドット状に高密度で２次元配列されてるため、この無機材料原子を種として合成、成長するカーボンナノチューブ１３は、隣り合うカーボンナノチューブ同志が極く近接して合成・成長しているため、互いのカーボンナノチューブ１３，１３・・・の存在により、垂直方向に成長する特性が向上する。

【００５５】一方、前述した、従来のカーボンナノチューブの固定・配列方法では、別途作製したカーボンナノチューブを配列・固定する際の種となる金属の配列が粗であるために、隣り合うカーボンナノチューブ同志が近接しておらず、従って本発明のような高密度に２次元的に成長する互いのカーボンナノチューブの存在による作用が生じることはなく、カーボンナノチューブが曲がる等して固定・配列される可能性が極めて高くなり、垂直配置の制御が困難となる。

【００５６】なお、上述した本発明における垂直方向への成長特性の傾向は、タンパク質分子４としてＤｐｓタンパク質を用いる場合、顕著となる。すなわち、Ｄｐｓタンパク質では、無機材料原子の大きさが４ｎｍ、間隔が９ｎｍとなり、垂直に配向する傾向がより一層強くなるからである。

【００５７】以上のように、本発明におけるカーボンナノチューブは、基板面に対して極めて良好に垂直配置しており、低電圧駆動の大電流電子線放出源として好ましく適用でき、例えば、フラットパネルディスプレイの電界放出型エミッタにおける冷陰極部材として好適に使用することができる。

【００５８】基板の両面にカーボンナノチューブが合成・成長しているものの場合、電子線放出源として両面を利用することもできるし、片面のみを利用してもよい。

【００５９】

【実施例】実施例１

タンパク質分子４として、内腔部に酸化鉄１を保持しているアポフェリチンを使用し、基板６としてシリコン基板を２枚使用し、図５に示す態様で、２枚の基板６のそれぞれに、アポフェリチン（２次元結晶）４を、高密度・高精度で展開配置し、図８（Ａ）に示す態様の基板６（但し、両面にアポフェリチン４が付着している）を２枚得た。

【００６０】なお、アポフェリチン溶液３は、生理食塩水中に、馬のひ臓から採取したアポフェリチンを濃度１００ｎｇ／ｍｌで含むものを使用し、シリコン基板６はそれぞれ、表面を１１０℃で紫外線による活性オゾンで親水性化処理したものを使用した。

【００６１】また、２枚の基板６は１つの容器１０内に一定の間隔をあけてそれぞれセットし、図示省略のシリンジを用い、アポフェリチン溶液３の容器１０からの抜出速度（液面低下速度）は０．１ｍｍ／分として、溶液３を抜き出した。

【００６２】上記のようにして得た２枚の基板６を、窒素ガス雰囲気中、４５０℃で、１時間保持して熱処理し、タンパク質部分２を焼失させて、図８（Ｂ）に示すような酸化鉄１を２次元的に、高密度のドット状で、（両面に）展開配置している基板６を２枚得た。

【００６３】この２枚の基板６の一方を更に、水素ガス雰囲気中、７００℃で、１時間保持して還元処理し、基板６の両面に展開配置している酸化鉄を還元して、鉄とした。

【００６４】上記２枚の基板６を、図７に示すＣＶＤ装置を用い、該装置内の密閉チャンバ２０内のヒータ２１上に、間隔を置いてそれぞれセットした。

【００６５】次いで、チャンバ２０内を真空ポンプ２２で排気し、パイプ２３からアルゴンガスをノズル２４を介してチャンバ２０内に導入して、チャンバ２０内を１Ｐａに保持しつつ、２枚の基板６をそれぞれ６００℃に加熱した。

【００６６】この後、切り替えバルブ２５を切り替え、供給装置２６からカーボン粒子源としてオルトメチルジアゾールケトンの蒸気をアルゴンガスに同伴させ、ノズル２４を介してチャンバ２０内に導入した。

【００６７】チャンバ２０内において、オルトメチルジアゾールケトンが分解してカーボン粒子が発生し、酸化鉄１を種として、図８（Ｃ）に示すように、２枚の基板６それぞれ（の両面）にカーボンナノチューブ１３を合成・成長させた。

【００６８】続いて、同じ密閉チャンバ２０内で、６００℃で１時間保持して、合成・成長したカーボンナノチューブ１３のアニーリング処理を行い、本発明におけるカーボンナノチューブを得た。

【００６９】上記のようにしてカーボンナノチューブ１１を合成・成長させ、アニーリング処理した２枚の基板６のそれぞれについて、電子放出テストを行った。

【００７０】このテストの条件および方法は、カーボンナノチューブを陰極とし、対極に白金コートしたチップを用い、電界として１０Ｖ／μｍ（＝10^6～10^7Ｖ／ｍ）を加えた。

【００７１】テストの結果は、２枚の基板とも、数ｍＡ／cm^2のオーダーの電流密度を得ることができた。

【００７２】

【発明の効果】以上のように、本発明のカーボンナノチューブでは、基板上に直接合成・成長させることができるばかりか、高密度・高精度での配列・固定および基板面への理想的な垂直配置が極めて容易である。

【００７３】これに伴い、低電圧駆動大電流電子線放出源としての良品質のカーボンナノチューブを、高い生産効率で、製造することができる。

【図面の簡単な説明】

【図１】タンパク質分子の構成を模式的に示す図

【図２】タンパク質分子の２次元的な配列・固定方法の一例を、工程順に示す説明図であり、

（Ａ）はタンパク質分子の分散液表面にポリペプチド膜を張り該液のｐＨを調節する工程を示す図

（Ｂ）はタンパク質分子がポリペプチド膜に付着してタンパク質分子の２次元結晶ができる工程を示す図

（Ｃ）はポリペプチド膜上に基板を載置して該膜を基板に付着させる工程を示す図

（Ｄ）はポリペプチド膜を介してタンパク質分子の２次元結晶が付着した基板を取り出した状態を示す図

【図３】タンパク質分子の２次元的な配列・固定方法の他の例を示す説明図

【図４】タンパク質分子の２次元的な配列・固定方法の更に他の例を示す説明図

【図５】タンパク質分子の２次元的な配列・固定方法の更に他の例を示す説明図であって、

（Ａ）がその方法を示す図

（Ｂ）がその方法で得られる濡れ膜を模式的に示す図

【図６】タンパク質分子の２次元的な配列・固定方法の更に他の例を、順を追って示す説明図

【図７】本発明におけるＣＶＤ法を実施する際に使用される装置を説明するための図

【図８】本発明のカーボンナノチューブの合成・成長方法の一例を、順を追って示す説明図であり、

（Ａ）が基板上にタンパク質分子を展開配置した状態を模式的に示す図

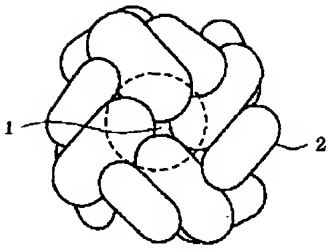
（Ｂ）がタンパク質分子のタンパク質部分を焼去し無機材料原子粒子とした状態を模式的に示す図

（Ｃ）が無機材料原子を種としてカーボンナノチューブを剛性・成長させた状態を模式的に示す図

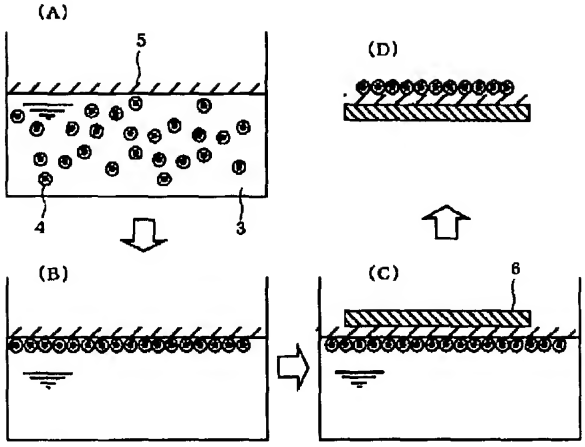
【符号の説明】

１　無機材料原子の芯
２　タンパク質の殻
３　タンパク質分子４を分散した緩衝液（溶液）
４　タンパク質分子
５　ポリペプチド膜
６　基板
７　濡れ膜
８　台
９　白金ブレード
１０　容器
１３　カーボンナノチューブ

【図1】



【図2】



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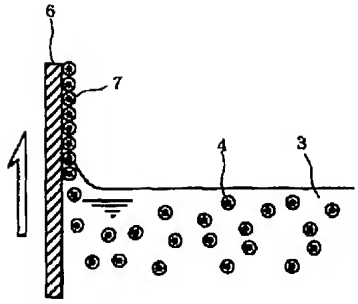
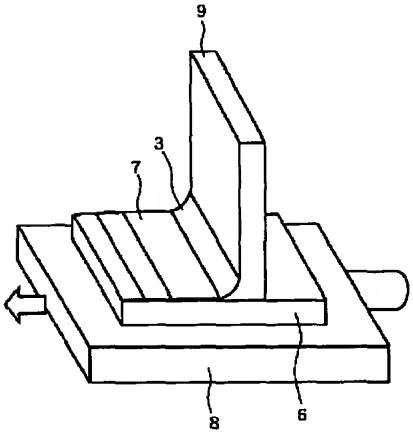


【図4】



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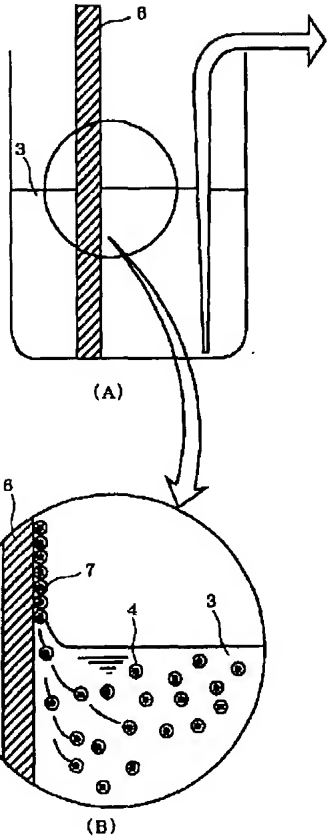
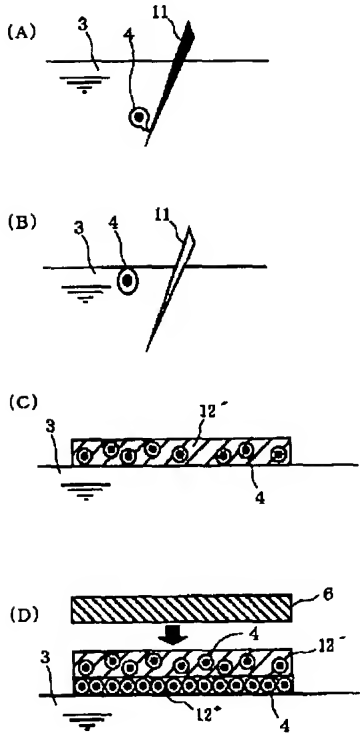
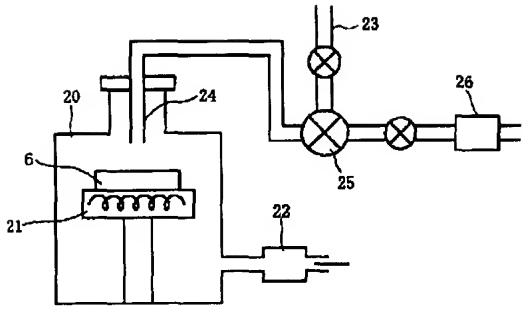


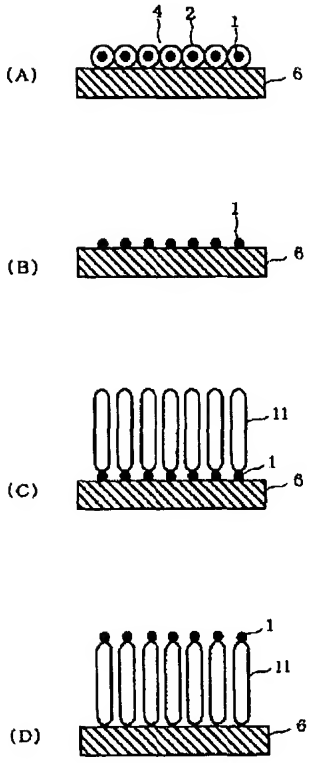
【図6】



【図7】



【図8】



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Bibliography.

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(51) [The 7th edition of International Patent Classification]

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C01B 31/02 101 .
C23C 16/02 .
H01J 1/304 .
9/02 .

[FI]

C23C 16/24 .
C01B 31/02 101 F .
C23C 16/02 .
H01J 9/02 B .
1/30 F .

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[Mode of Application] OL.
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(22) [Filing Date] December 21, Heisei 11 (1999. 12.21)
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[Identification Number] 100097445.
[Patent Attorney]
[Name] Iwahashi Fumio (besides two persons)
[Theme code (reference)]

4G046.

4K030.

[F term (reference)]

4G046 CA02 CB01 CB09 CC06.
4K030 AA09 bus-available27 BB11 CA01 CA18 DA09 FA10 LA11.

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Summary.

---

(57) [Abstract]
[Technical problem] It direct-compounds and grows up, and moreover, it is highly precise and a substrate front face is provided with high density and the arranged carbon nanotube.
[Means for Solution] It is the molecule 4 which covered the circumference of owner Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. for the lumen in protein 2, and after carrying out expansion arrangement of this molecule that made the inorganic-material atom 1 hold in the aforementioned lumen section substrate top 6, it is the carbon nanotube 13 which comes as a seed to compound the aforementioned inorganic-material atom 1 which remains on a substrate by removing this protein. The protein molecule 4 may be a virus, a ferritin family (a ferritin and apoferritin), DpsA protein, or MrgA protein, the inorganic-material atom 1 may be either of the cobalt compounds, such as nickel compounds, such as iron compounds, such as iron and a ferric acid ghost, nickel, and a nickel oxide, cobalt, and a cobalt oxide, and a synthetic method may be CVD.

[Translation done.]

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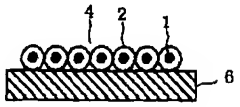

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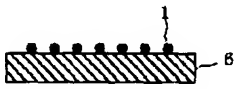

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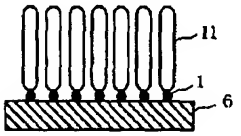

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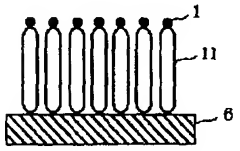

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CLAIMS

[Claim(s)]
[Claim 1] The carbon nanotube which comes as a seed to compound the aforementioned inorganic-material atom which remains on a substrate by removing the aforementioned protein after carrying out expansion arrangement of the aforementioned molecule which it is [molecule] the molecule which has a lumen and covered the circumference in protein, and made the inorganic-material atom hold in the aforementioned lumen section on a substrate.
[Claim 2] The carbon nanotube according to claim 1 characterized by a protein molecule being a virus.
[Claim 3] The carbon nanotube according to claim 1 characterized by a protein molecule being a ferritin family.
[Claim 4] The carbon nanotube according to claim 3 characterized by a ferritin family being a ferritin or an apoferritin.
[Claim 5] The carbon nanotube according to claim 1 characterized by a protein molecule being DpsA protein or MrgA protein.
[Claim 6] The carbon nanotube according to claim 1 to 5 characterized by an inorganic-material atom being any one sort of iron, a ferric acid ghost, other iron compounds, nickel, a nickel oxide, other nickel compounds, cobalt, a cobalt oxide, and the other cobalt compounds.

[Claim 7] The carbon nanotube according to claim 1 to 6 characterized by a synthetic method being CVD.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] About a carbon nanotube, especially this invention is high-density on a substrate front face, and relates to the carbon nanotube moreover arranged with high degree of accuracy.
[0002]
[Description of the Prior Art] Since the radius of curvature at a nose of cam is small, a carbon nanotube is suitable as a component (cold cathode material) of the source of electron emission in an electrolysis discharge type electronic emitter (cold cathode equipment), while having a high aspect ratio.
[0003] For example, it is reported that the high emission current density called 400microA/cm2 is obtained from the carbon nanotube which bundled many books on low turn-on voltage called 64V.
[0004] Thus, some proposals and reports of the synthetic technology, applied technology, etc. till today are made.
[carbon nanotube / with which the application as a high current electron ray emitter of a low-battery drive attracts attention]
[0005] For example, it is desirable to carry out orientation at right angles to an electrode side, if a carbon nanotube is made by carrying out orientation as much as possible in order to apply the field emission type emitter which uses a carbon nanotube as a cold cathode member to a flat-panel display, and if it can do, it is desirable to arrange in the shape of a two dimensional array corresponding to a fluorescent substance. There are following reports and proposals about this array technology.
[0006] Walt de Heer et In the Science magazine 268 volume (1995) 845 page by al., pass the suspension of a carbon nanotube to a ceramic filter, a filter front face is made to arrange a carbon nanotube, this is imprinted on a sheet plastic, and the technology which forms the layer of the carbon nanotube which carried out orientation into the field perpendicular or the field on this sheet is indicated.
[0007] Moreover, JP,10-149760,A is indicating the technology which uses a carbon nanotube as electron-emitter material in field emission type cold cathode equipment. Hit forming two or more electron emitters on a support substrate, for example, arc discharge is made to sublimate the carbon of an anode electrode. An application, distribution, etc. carry out the carbon nanotube which it was deposited on the cathode and formed it, and as fallen trees overlap, when they make it arrange on a substrate, the technology which constitutes each electron emitter is indicated.
[0008] JP,10-12124,A is indicating the technology of making it growing up by the operation of a metal catalyst which deposited the carbon nanotube used as an electron emitter in the pore regularly arranged into the oxide film on anode.
[0009] Furthermore, the technology which the carbon nanotube operated as a field emission type electronic emitter is

made to arrange in the direction of impression electric field by the electrophoresis method, is made to move it to the attachment component which consists of polysilane formed on the substrate, and is fixed is indicated Japanese painting image society (The Society of Electrophotography of Japan) issue "Pan-Pacific Imaging Conference/Japan Hardcopy '98" (15-July 17, 1998 holding) 313-316 page.

[0010]

[Problem(s) to be Solved by the Invention] However, each the above report and proposal produce the carbon nanotube separately, and are the technology which arranges and fixes this on a substrate, and productivity carries out orientation on about [that it cannot necessarily be called fitness] and a substrate and is high-density [a proposal]. And an array and fixation with high degree of accuracy cannot necessarily be referred to as easy, and there is a problem plentifully also about the vertical disposition to a substrate side ideal as an electron ray emitter (to for example, request positions, such as arrangement of the shape of a two dimensional array the fluorescent substance was made to correspond).

[0011] this invention is a carbon nanotube directly compounded on a substrate, and, moreover, aims at the composition offering the carbon nanotube which can realize easily ideal vertical disposition to an array and fixation with the high density and high degree of accuracy of a carbon nanotube, and a substrate side.

[0012]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the carbon nanotube of this invention holds an inorganic-material atom in the lumen section, after it carries out expansion arrangement of the molecule which covered the circumference in protein on a substrate, by removing protein, compounds as a seed the inorganic-material atom which remains on a substrate, and is characterized by the bird clapper.

[0013] The carbon nanotube of this invention moreover, the protein molecule of (1) above ** a virus (for example, an adenovirus, a rotavirus, and a poliovirus --) A ferritin family like ** ferritins, such as HK97 and CCMV, or an apoferritin, ** May be DpsA protein and MrgA protein (refer to protein data bank), and (2) The above-mentioned inorganic-material atom may be any one sort of iron, a ferric acid ghost, other iron compounds, nickel, a nickel oxide, other nickel compounds, cobalt, a cobalt oxide, and the other cobalt compounds, and the synthetic method of (3) above may be CVD.

[0014]

[Embodiments of the Invention] In this invention, on a substrate, it is high degree of accuracy (in this invention, when describing it as "high degree of accuracy", it means "it is high degree of accuracy to a request position"), and expansion arrangement (namely, two-dimensional an array and fixation) of the molecule (it may be hereafter described as a "protein molecule") which held the inorganic-material atom in the lumen section, and covered the circumference in protein first is carried out in high density and a request position.

[0015] As typically shown in drawing 1 , this protein molecule holds the heart 1 of an inorganic-material atom in the lumen section, it is the metalloprotein complex which covered this circumference with the proteinic husks 2, and the ferritin taken out from internal organs, such as a spleen of animals, such as a horse and a cow, and liver, the apoferritin which connoted various kinds of inorganic-material atoms to the lumen can use it preferably.

[0016] In the case of a ferritin, the inorganic-material atom of the heart 1 is usually an iron oxide (Fe 2O3), the total of about 6nm and an iron oxide of the diameter of the heart 1 is about 3000 pieces, husks 2 are 24 **** of with a molecular weight of about 20,000 protein, and the outer diameter of the whole 24 **** is about 12nm.

[0017] Although illustration omits in the case of Dps protein, the diameter of the heart 1 is about 4nm, husks 2 are 12 **** of a regular tetrahedron, and the outer diameter of the whole 12 **** is about 9nm.

[0018] In addition, in this invention, the inorganic-material atom of the heart 1 may not be limited to an iron oxide, but may be iron compounds other than iron and an iron oxide or nickel, cobalt, these oxides, compounds other than an oxide, etc.

[0019] Two-dimensional array and fixation of this protein molecule are performed to JP,11-45990,A by the method of a publication.

[0020] Specifically, as shown in drawing 2 , the polypeptide film 5 is stretched on the front face of the buffer solutions (solution) (equivalent mixed solution of concentration 40mM, the phosphoric-acid buffer solution of pH 5.3, and the

sodium chloride solution of concentration 40mM etc.) 3 which distributed the protein molecule 4, and pH of the buffer solution 3 is adjusted on it (drawing 2 (A)). Since the protein molecule 4 wears the negative charge to the polypeptide film 5 wearing the positive charge, in connection with the passage of time, the protein molecule 4 adheres to the polypeptide film 5, and the two-dimensional crystal of the protein molecule 4 is made (drawing 2 (B)).

[0021] A substrate 6 is laid on this polypeptide film 5, and ** (appear) and the polypeptide film 5 are made to adhere to a substrate 6 (drawing 2 (C)). If this substrate 6 is taken out, the substrate 6 to which the two-dimensional crystal of the protein molecule 4 adhered can be obtained through the polypeptide film 5 (drawing 2 (D)).

[0022] Or if a substrate 6 is put into the solutions (what added electrolyte matter, such as a sodium chloride, to pure water and pure water) 3 which distributed the protein molecule 4 and this substrate 6 is gradually pulled up at right angles to an oil level as shown in drawing 3 , it will get wet to both sides of a substrate 6, and a film 7 will arise. Since [this] it gets wet and the protein molecule 4 is distributing in the shape of two-dimensional on the film 7, if a film 7 dries, the two-dimensional crystal of the protein molecule 4 can obtain the substrate 6 adhering to both sides.

[0023] Moreover, as shown in drawing 4 , the platinum blade 9 is perpendicularly stood on the substrate 6 placed on the base 8, the solution 3 which distributed the same protein molecule as the case of drawing 2 between the substrate 6 and the blade 9 is given with surface tension, and if it fixes and moves in the direction of an arrow gradually by constant speed in a base 8 6, i.e., a substrate, the thin film 7 of a solution 3 will generate a blade 9 on a substrate 6. In this thin film 7, since the protein molecule 4 is distributing in the shape of two-dimensional, if a film 7 dries, the two-dimensional crystal of the protein molecule 4 can obtain the substrate 6 adhering to one field.

[0024] Furthermore, it is perpendicular (although illustration is omitted) to a solution 3 about a substrate 6 in the container 10 which poured in the solution 3 which distributed the same protein molecule 4 as the case of drawing 2 as shown in drawing 5 (A). Even when it is slanting, it is good, and a solution 3 is gradually extracted by constant speed by the syringe (illustration ellipsis) etc. from the upper part of a container 10 (although illustration is omitted). The hole is vacated under the container 10, as it indicates drawing 5 (B) that you may extract gradually by constant speed by operation of gravity etc. from this hole, it gets wet to both sides of a substrate 6, and a film 7 arises. Since [this] it gets wet, it gets wet in the case of drawing 2 on a film 7 and the protein molecule 4 is distributing in the shape of two-dimensional like a film 7, if a film 7 dries, the two-dimensional crystal of the protein molecule 4 can obtain the substrate 6 adhering to both sides.

[0025] In the method shown in these drawing 2 -5 the two-dimensional crystal of the protein molecule 4 You may form all over a substrate 6 and may form only in a specific portion by the proper pattern. in the case of the latter The field where the protein molecule 4 tends to adhere to substrate 6 front face beforehand, and the field which cannot adhere easily (for example, by the art mentioned later) After creating the hydrophobic field and the hydrophilic field or making the protein molecule 4 adhere to a substrate 6 in the shape of two-dimensional, the method of a proper pattern removing this molecule 4 is adopted.

[0026] Moreover, even if it is a method by the replica method (Adv.Biophys.Vol.34, 99 to p107 (1987) reference) developed by Yoshimura and others as shows drawing 6 (A) - (D), the two-dimensional crystal film of the protein molecule 4 can be obtained.

[0027] First, in drawing 6 (A), in the specific solution (sucrose solution of 2% of concentration) 3, the protein molecule (apoferritin which connoted the iron oxide) 4 is risen to surface on the sucrose solution 3, as the protein molecule 4 shows it at drawing 6 (B), when syringe 11 grade is used and poured in.

[0028] The protein molecule 4 which reached the gas-liquid interface first forms amorphous film 12', as shown in drawing 6 (C), and the protein molecule 4 which reached later adheres to the bottom of this film 12', and as shown in drawing 6 (D), it forms 12" of two-dimensional crystals in the bottom of this film 12'.

[0029] If a substrate 6 is laid on the film 12 which consists of this amorphous film 12' and 12" of two-dimensional crystals as shown in drawing 6 (D), the film 12 of this protein molecule will be imprinted at a substrate 6 side.

[0030] This film 12 can imprint a substrate 6 to a substrate 6 side easily by processing hydrophobic.

[0031] Hydrophobic processing of a substrate 6 can be performed by the silicon substrate by carrying out processing by the hexamethyldisilazane (HMDS (CH3)) (3SiNHSi3 (CH3)) etc., or covering by the monomolecular film of carbon fluoride in a glass substrate etc.

[0032] Also in this replica method, the proteinic two-dimensional crystal film 12 may be formed all over a substrate 6, and if conditions are selected, since a film 12 is imprinted only to a hydrophobic field and it can avoid imprinting in a hydrophilic field, can form a hydrophobic field and a hydrophilic field by the proper pattern on a substrate 6 beforehand, and can create a film 12 to a proper pattern.

[0033] After carrying out expansion arrangement of the protein molecule on a substrate by the two-dimensional crystallized state as mentioned above, a protein portion is removed and the inorganic-material atom made to hold in the lumen section of a protein molecule is made to appear two-dimensional on a substrate in this invention.

[0034] Generally heat treatment performs removal of this protein portion.

[0035] For example, proper time (for example, 1 hour) maintenance, then the polypeptide film in the case of a protein portion or drawing 2 are burned down by inert gas Naka, such as nitrogen, and 400-500 degrees C, and an inorganic-material atom remains by the shape of a high-density dot two-dimensional on a substrate.

[0036] still more proper [at the inside of reducing-gas atmosphere, such as hydrogen, and 500-900 degrees C] in this -- time maintenance may be carried out and an inorganic-material atom may be returned

[0037] The carbon nanotube of this invention is directly compounded on a substrate by using as a seed the inorganic-material atom (it being a meaning containing the oxide and other compounds in this invention, when describing it as an "inorganic-material atom") which carried out expansion arrangement on the substrate as mentioned above.

[0038] Although what method is sufficient as this synthetic method as long as a carbon nanotube is compoundable, CVD can apply it preferably.

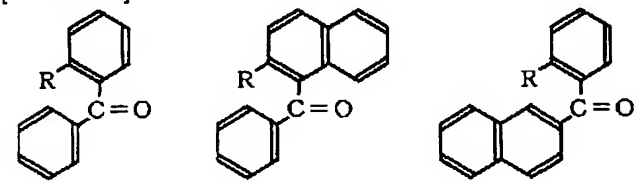
[0039] That is, the substrate which carried out expansion arrangement of the inorganic-material atom is placed into a sealing system, the organic compound used as the raw material of a carbon nanotube is introduced in this sealing system, and substrate temperature is made into 500-900 degrees C. By this, an organic compound decomposes, a carbon particle occurs, this carbon particle uses an inorganic-material atom as a seed, and a carbon nanotube is compounded and is grown up.

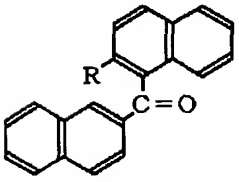
[0040] The CVD in this invention can also be performed under reduced pressure (for example, less than 1Pa - about 10 - 6Pa).

[0041] Moreover, if it is an organic compound, although it will not be especially limited as a source of carbon, the aromatic-ketone compound shown in ** 1, an ortho methyl diazole ketone, a phthalocyanine, other aromatic compounds or various kinds of aliphatic compounds, etc. can use it preferably.

[0042]

[Formula 1]





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[0043] This CVD is performed using equipment as shown in drawing 7 .

[0044] or -- in drawing 7 , a substrate 6 is set on the heater 21 in the sealing chamber 20, and a substrate 6 is heated at a heater 21, introducing inert gas, such as nitrogen and an argon, from a nozzle 24 from a pipe 23, exhausting and decompressing the inside of a chamber 20 with a vacuum pump 22

[0045] After the temperature of a substrate 6 is stabilized, the change bulb 25 is operated, and the steam of the above

organic compounds is made to accompany to carrier gas, such as nitrogen and an argon, from the source feeder 26 of carbon, and it supplies in the sealing chamber 20, and leads on a substrate 6 by the nozzle 24.

[0046] It decomposes [near the substrate 6 top], and the steam of this organic compound generates a carbon particle, and compounds and grows up a carbon nanotube by using the inorganic-material atom on a substrate 6 as a seed.

[0047] What is necessary is to take out from this chamber in the same sealing chamber, to hold for about 1 hour and just to perform annealing of a carbon nanotube by 400-900 degrees C among inert gas atmosphere, such as nitrogen and an argon, with a proper heating means, by the above-mentioned CVD, after compounding and growing up a carbon nanotube by using an inorganic-material atom as a seed. While adhesion with the inorganic-material atom used as a seed becomes good with this annealing, improvement in electric conductivity can be aimed at.

[0048] Order is typically shown for the situation of composition and growth of the carbon nanotube in this invention explained above in drawing 8 later on.

[0049] First, as shown in drawing 8 (A), on a substrate 6, it is high-density and highly precise and expansion arrangement of the protein molecule 4 (two-dimensional crystal) is carried out.

[0050] Subsequently, it is high-density and highly precise and the inorganic-material atom 1 currently held at the lumen section of this molecule 4 is made to remain in the shape of a dot two-dimensional on a substrate 6, as this substrate 6 is heat-treated, the protein portion 2 of the protein molecule 4 is ****(ed) and it is shown in drawing 8 (B).

[0051] The substrate 6 of this state is placed into a sealing system, and by CVD, if a carbon steam is made to **** in this system, a carbon nanotube 13 will compound and grow by using the inorganic-material atom 1 on a substrate 6 as a seed. The growth direction has a down case, as are shown in drawing 8 (C) and it is shown in an above case and drawing 8 (D).

[0052] Annealing processing of this is carried out with a proper heating means, and the carbon nanotube of this invention is obtained.

[0053] In addition, although drawing 8 showed the mode in which the protein molecule 4 and the inorganic-material atom 1 adhere to one side of a substrate 6, and a carbon nanotube 13 compounds and grows, these [4 and 1] adhere to both sides of a substrate 6, and a carbon nanotube 13 may compound and grow.

[0054] Thus, an adjacent carbon nanotube comrade does **** proximity, and composition and since it is growing up, the carbon nanotubes 13 which use this inorganic-material atom as a seed since two-dimensional array of the inorganic-material atom (6nm) by which expansion arrangement is carried out is carried out to the 6th page of a substrate by high density at the predetermined intervals (about 12nm interval) in this invention at the shape of a dot, and compound and grow are the mutual carbon nanotubes 13 and 13... The property of growing up perpendicularly improves by existence.

[0055] On the other hand by the fixation / array method of the conventional carbon nanotube mentioned above The array of the metal used as the kind at the time of arranging and fixing the carbon nanotube produced separately to a rough ****** sake An adjacent carbon nanotube comrade does not approach, therefore the operation by existence of a mutual carbon nanotube like this invention which grows two-dimensional with high density does not arise. It carries out that a carbon nanotube bends etc., and fixation and possibility of being arranged become very high and control of vertical disposition becomes difficult.

[0056] In addition, the inclination of the growth property to the perpendicular direction in this invention mentioned above becomes remarkable when using Dps protein as a protein molecule 4. That is, it is because the size of an inorganic-material atom is set to 4nm, an interval is set to 9nm and the inclination which carries out orientation perpendicularly becomes still stronger in Dps protein.

[0057] As mentioned above, vertical disposition of the carbon nanotube in this invention is carried out very good to the substrate side, and it can be preferably applied as a high current electron ray emitter of a low-battery drive, for example, can be suitably used as a cold cathode member in the field emission type emitter of a flat-panel display.

[0058] When a carbon nanotube is what is compounding and growing, both sides can also be used for both sides of a substrate as an electron ray emitter, and only one side may be used for them.

[0059]

[Example] As an example 1 protein molecule 4, the apoferritin holding the iron oxide 1 was used for the lumen section, two silicon substrates were used as a substrate 6, in the mode shown in drawing 5 , to each of two substrates 6, it was high-density and highly precise, expansion arrangement of the apoferritin (two-dimensional crystal) 4 was carried out, and two substrates 6 (however, the apoferritin 4 has adhered to both sides) of a mode shown at drawing 8 (A) were obtained.

[0060] In addition, what contains the apoferritin extracted from the spleen of a horse by 100 ng/ml concentration in a physiological saline was used for the apoferritin solution 3, and the silicon substrate 6 used what hydrophilic-property--ization-processed the front face for the activity ozone by ultraviolet rays by 110 degrees C, respectively.

[0061] Moreover, two substrates 6 opened the fixed interval into one container 10, and set it, respectively, and the extraction speed (oil-level fall speed) from the container 10 of the apoferritin solution 3 extracted the solution 3 as a part for 0.1mm/using the syringe of an illustration abbreviation.

[0062] Among nitrogen gas atmosphere, held two substrates 6 obtained as mentioned above for 1 hour, heat-treated them at 450 degrees C, the protein portion 2 was made burned down, and two substrates 6 which are carrying out expansion (to both sides) arrangement of the iron oxide 1 as shown in drawing 8 (B) by the shape of a high-density dot two-dimensional were obtained.

[0063] One side of these two substrates 6 was further held at 700 degrees C among hydrogen gas atmosphere for 1 hour, and reduction processing was carried out, and the iron oxide which is carrying out expansion arrangement was returned to both sides of a substrate 6, and it considered as iron.

[0064] Using the CVD system which shows two above-mentioned substrates 6 to drawing 7 , on the heater 21 in the sealing chamber 20 in this equipment, the interval was kept and it set, respectively.

[0065] Subsequently, two substrates 6 were heated at 600 degrees C, respectively, having exhausted the inside of a chamber 20 with the vacuum pump 22, having introduced argon gas in the chamber 20 through the nozzle 24 from the pipe 23, and holding the inside of a chamber 20 to 1Pa.

[0066] Then, changed the change bulb 25, the steam of an ortho methyl diazole ketone was made to accompany to argon gas as a source of a carbon particle from a feeder 26, and it introduced in the chamber 20 through the nozzle 24.

[0067] an ortho methyl diazole ketone decomposes in a chamber 20, a carbon particle occurs, and it is shown in drawing 8 (C) by using an iron oxide 1 as a seed -- as -- two substrates 6 -- the carbon nanotube 13 was compounded and grown up, respectively (both sides)

[0068] Then, within the same sealing chamber 20, it held at 600 degrees C for 1 hour, composition and annealing processing of a carbon nanotube 13 in which it grew up were performed, and the carbon nanotube in this invention was obtained.

[0069] It compounded as mentioned above, the carbon nanotube 11 was grown up, and the electron emission test was performed about each of two substrates 6 which carried out annealing processing.

[0070] The conditions and method of this test added micrometer in 10v (=106 - 107 V/m) /as electric field using the chip which used the carbon nanotube as cathode and carried out the platinum coat to the counter electrode.

[0071] As for the result of a test, two substrates were able to obtain the current density of the order of several mA/cm2.

[0072]

[Effect of the Invention] As mentioned above, the ideal vertical disposition to an array and fixation with about [that it can direct-compound and can be made to grow up on a substrate in the carbon nanotube of this invention], and high density and high degree of accuracy, and a substrate side is very easy.

[0073] In connection with this, the carbon nanotube of the quality of an excellent article as a low-battery drive high current electron ray emitter can be manufactured with high productive efficiency.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing showing the composition of a protein molecule typically
[Drawing 2] It is explanatory drawing showing an example of the two-dimensional array / fixed method of a protein molecule in order of a process.
(A) is drawing showing the process which stretches a polypeptide film on the distributed liquid front face of a protein molecule, and adjusts pH of this liquid.
(B) is drawing showing the process which a protein molecule adheres to a polypeptide film and can do the two-dimensional crystal of a protein molecule.
(C) is drawing showing the process which a substrate is laid [process] on a polypeptide film and makes this film adhere to a substrate.
(D) is drawing showing the state where the substrate to which the two-dimensional crystal of a protein molecule adhered through the polypeptide film was taken out.
[Drawing 3] Explanatory drawing showing other examples of the two-dimensional array / fixed method of a protein molecule
[Drawing 4] Explanatory drawing showing the example of further others of the two-dimensional array / fixed method of a protein molecule
[Drawing 5] It is explanatory drawing showing the example of further others of the two-dimensional array / fixed method of a protein molecule.
Drawing in which (A) shows the method
Drawing where (B) is obtained by the method and in which getting wet and showing a film typically
[Drawing 6] Explanatory drawing showing order for the example of further others of the two-dimensional array / fixed method of a protein molecule later on
[Drawing 7] Drawing for explaining the equipment used in case the CVD in this invention is enforced
[Drawing 8] It is explanatory drawing showing order for an example of the composition / growth method of the carbon nanotube of this invention later on.
Drawing showing typically the state where (A) carried out expansion arrangement of the protein molecule on the substrate
Drawing showing typically the state where (B) ****(ed) the protein portion of a protein molecule and considered as the inorganic-material atom particle
Drawing in which (C's) using an inorganic-material atom as a seed, and showing typically rigidity and the state where it was made to grow up for a carbon nanotube
[Description of Notations]
1 Heart of Inorganic-Material Atom
2 Proteinic Husks
3 Buffer Solution Which Distributed Protein Molecule 4 (Solution)
4 Protein Molecule
5 Polypeptide Film

6 Substrate
7 Get Wet and it is Film.
8 Base
9 Platinum Blade
10 Container
13 Carbon Nanotube

[Translation done.]

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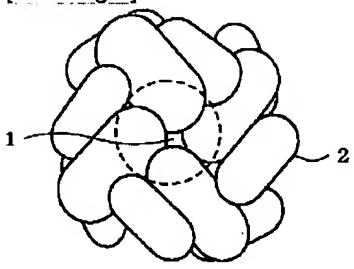
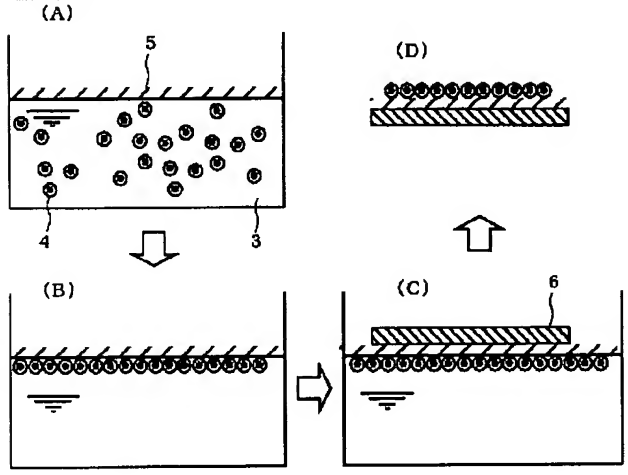
DRAWINGS

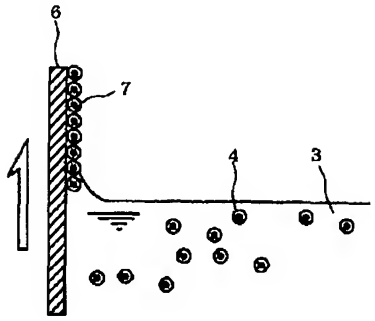
[Drawing 1]



[Drawing 2]



[Drawing 3]



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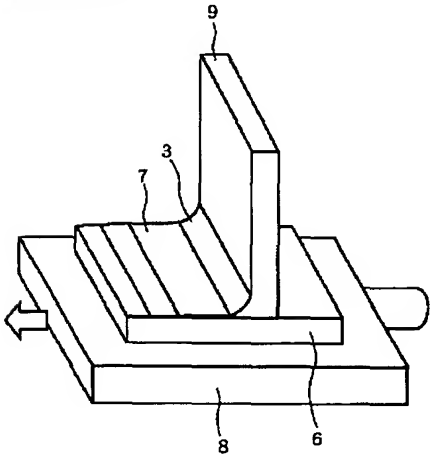

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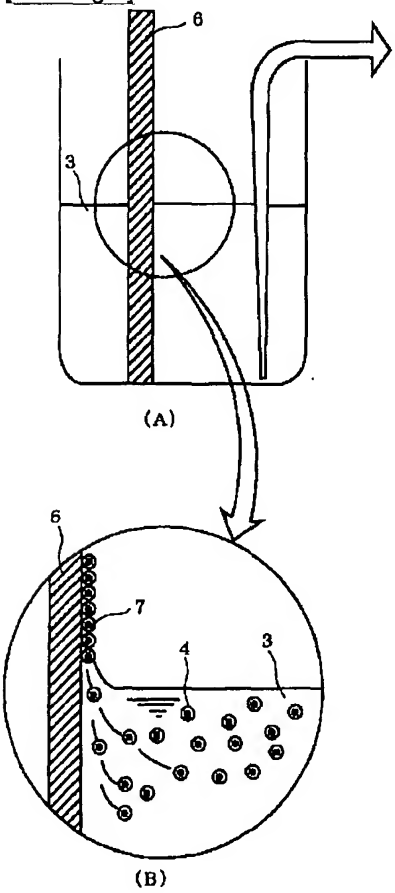

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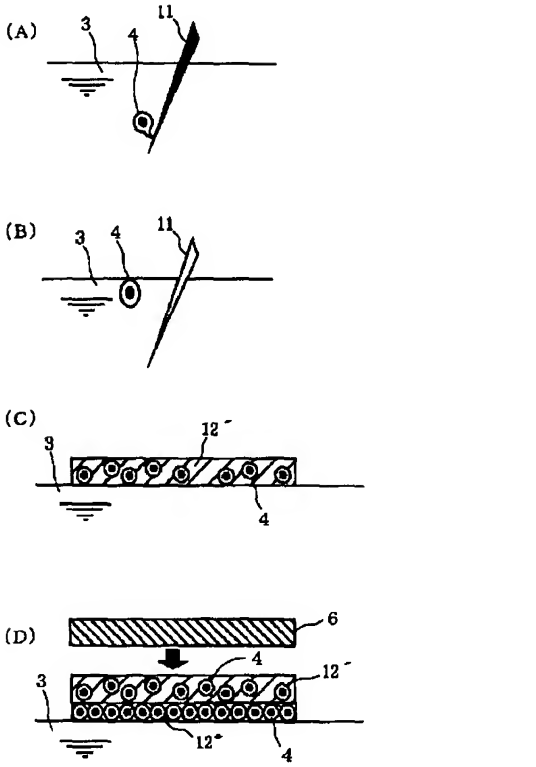
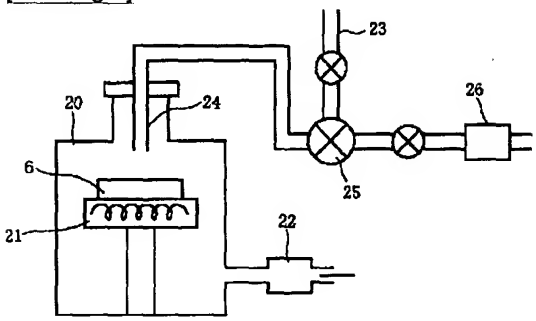
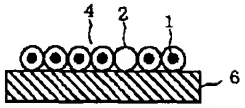


[Drawing 7]



[Drawing 8]

(A)



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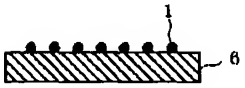

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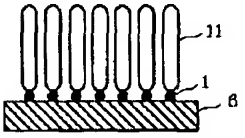

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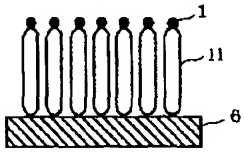

[Translation done.]